Extended lifetime of fluoride optics

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ABSTRACT

Surface and coating technology plays an important role for extending lifetime of fluoride optics for ArF excimer laser applications. Optically finished CaF_2 optics is characterized as top surface and subsurface by means of non-distractive quasi-Brewster angle technique. The subsurface is revealed by removing the top surface via distractive methods. Color centers on plasma ion and laser irradiated CaF_2 optics are discussed. The results suggest that fluorine depletion is associated with laser damage, dense smooth coatings enable one to extend the lifetime of CaF_2 optics.

Keywords: CaF_2, subsurface damage, color center, F-doped SiO_2 film, ArF laser optics.

1. INTRODUCTION

Advanced optical lithography has been extensively used to mass-produce patterned silicon wafers in semiconductor manufacturing. As semiconductor processing is progressed from the 65nm to the 45nm node and beyond, the applications of ArF excimer laser with increasing power and repetition rate require low loss, environmental stable and laser durable calcium fluoride optics (CaF_2) for laser optics and precision optics, where surface quality and surface mitigation techniques play a critical role. Advanced surface finishing and cleaning include the evaluation of CaF_2 surfaces with various finishing processes from optical polishing;[1-3] magnetorheological finishing (MRF);[4] diamond turning;[5] ultrasonic and ultraviolet ozone cleaning;[6] in-situ plasma ion cleaning.[7] Fundamental understanding of film growth of fluoride materials and plasma ion interaction with oxide materials enables one to mitigate CaF_2 surface and extend lifetime of CaF_2 based optics.[8-13]

In this paper, the top surface and subsurface of optically polished CaF_2 (111) are evaluated via different techniques, including non-distractive quasi-Brewster angle technique, magnetorheological finishing (MRF) iteration and etching processes. Surface quality of various CaF_2 is compared by means of low-energy-plasma-ion bombardment. The plasma generated color centers on CaF_2 are compared to the laser induced. Dense and smooth coatings are employed to prevent fluorine depletion and enhance the performance of CaF_2 optics.

2. SURFACE AND SUBSURFACE

Like most ionic crystals, CaF_2 is prone to chipping and cleavage during optical finishing process such as mechanical cutting and grinding operations etc. The mechanical operations necessary to

shape the optics, leave behind deep fractures or subsurface damage which have to be further removed by the subsequent micro-grinding, polishing and super polishing steps in optical finishing. The subsurface damage (SSD), in general, is referred to a distorted layer near the crystal surface, resulting from a brittle material removal process, and from high stress normal to the surface during optical finishing process. In many applications, SSD can be the cause of system failure, and it must therefore, be removed from surfaces. Accurate determination of SSD is critical for high quality optical surfaces, such as those intended for ArF excimer laser optics and precision optics.
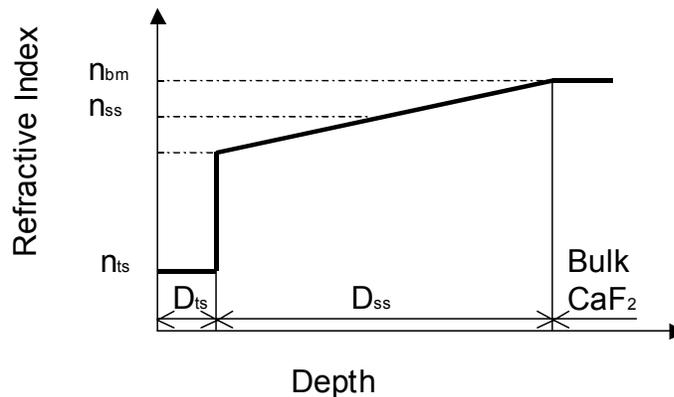
Fig. 1 Schematic of refractive index depth profile of an optically finished CaF_2, including a layer of top surface (D_{ts}) and subsurface (D_{ss}).

Fig. 1 schematically plots the refractive index depth profile of an optically finished CaF_2. The optically finished CaF_2 surface can be considered as the combination of a top surface (D_{ts}) and a subsurface (D_{ss}) with microscopic fractures and high density of crystal dislocations. The top surface is proportional to surface root-mean-square roughness (RMS). The subsurface represents the depth of the distorted layer with a mean refractive index of n_{ss}, which is less than the refractive index of the bulk CaF_2 n_{bm}. The significant physical difference of the top surface and the subsurface enables one to separate their contributions to the behavior of the quasi-Brewster angle, [3,5,6] i.e., the slope of the quasi-Brewster angle is dominated by the top surface, while the displacement of the quasi-Brewster angle is determined by the subsurface. Since the quasi-Brewster angle is a function of wavelength, an experimental determination of the quasi-Brewster angle shift at various wavelengths enables one to calculate the average refractive index, and to estimate the depth of SSD on optically polished CaF_2. The estimated subsurface damage may extend to a few hundreds of nanometers, depending upon the setup of optical finishing processes.

The top surface and subsurface of optically polished CaF_2 (111) can also be separated by means of MRF iteration.[6] The subsurface roughness σ can be considered as an addition of the contributions of SSD σ_{SSD} and MRF σ_{MRF}, i.e.,

$$\sigma = \sigma_{SSD} + \sigma_{MRF} \qquad (1)$$

Fig. 2 plots the surface roughness evolution after MRF iterating an optically polished CaF$_2$ (111) surface, along with inserted AFM images. Beginning with a top surface roughness of 0.44nm in RMS, the microroughness rises to 1.92nm after the first 50nm of MRF removal. After additional MRF removals, the RMS drops to 0.54nm for 200nm total removal, and then decreases slightly as the total MRF removal approaches 600nm. The inserted AFM images represent the top surface, the subsurface of 50nm and 600nm in depth, respectively. Based on Eq.(1), the final RMS is intrinsic to the MRF process σ_{MRF}, dominated by directional structure as shown in the corresponding AFM image.
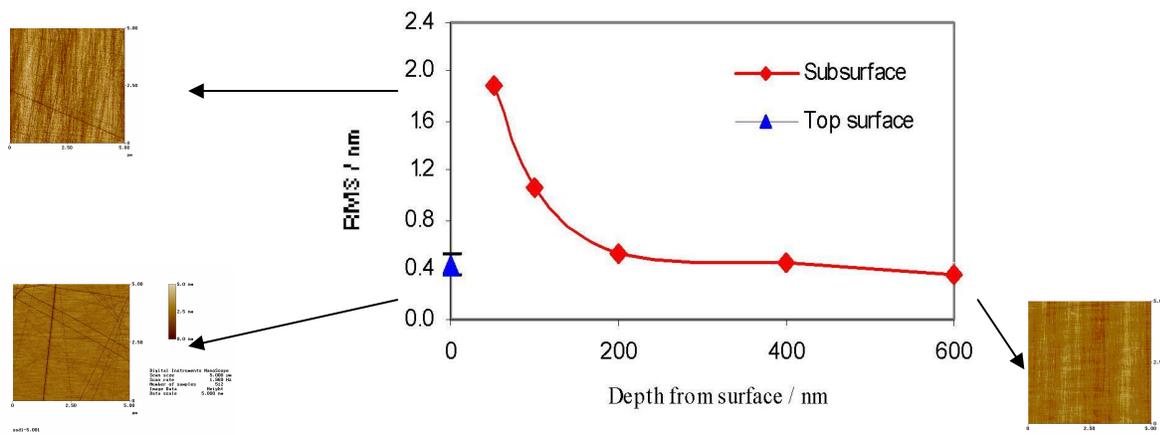
Fig. 2. Evolution of surface roughness RMS measured after MRF revealing the subsurface character of an optically polished CaF$_2$ (111), along with inserted AFM images.
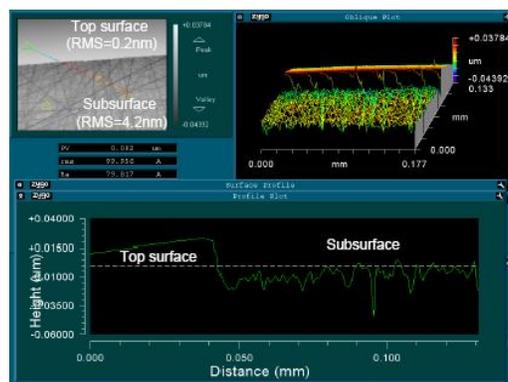
Fig. 3 Top surface and subsurface of an optically polished CaF$_2$ (111).

Fig. 3 shows the image of both the top surface and the subsurface by partially removal of 50nm from an optically polished CaF$_2$ (111) surface. The measured top surface is 0.2nm in RMS measured by using ZYGO New View 5000. The surface roughness increases to 4.2nm on the subsurface of 50nm in depth. The subsurface damage is clearly shown in the removal area.

3. SURFACE AND COLOR CONTER FORMATION

It has been reported that CaF_2 surfaces are susceptible to fluorine loss when exposed to energetic radiation.[13-16] Fluorine depletion leads to color center formation depending upon surface quality of CaF_2.[7] Fig. 4 depicts the spectral transmittance of a CaF_2 window before and after Ar^+ plasma ion bombardment. Strong absorption around 580nm corresponds to calcium colloid formation. A weak broad absorption ranging from 400nm down to 300nm represents the combined contributions of F center (an electron trapped at an anion vacancy), V_k center (hole binding two anions to a F_2^- molecule) and H center (a fluorine atom at an interstitial site covalently bound to a lattice anion), peaking at 374nm, 316nm and 306nm respectively.[14-16] The colloid formation results from aggregation of F centers, a process favored in CaF_2 by the good match between the lattice structure and atomic spacing of calcium metal and the Ca^{2+} sublattice in CaF_2.[16] The momentum transfer during plasma ion bombardment further promotes the colloid formation, leading to a sharp absorption peak at 580nm.
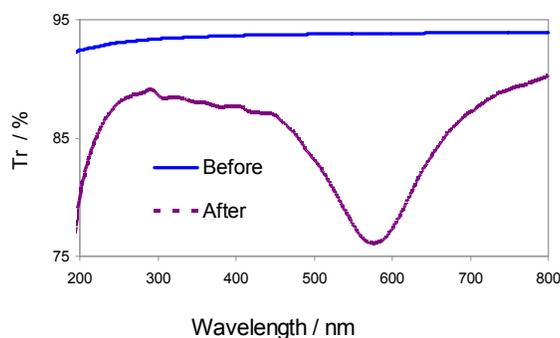
Fig. 4 Spectral transmittance of CaF_2 window before and after Ar^+ plasma ion bombardment.

Fig. 5 shows the calcium colloid related peak absorption, generated by low energy plasma ion on an optically finished CaF_2 (111) surface, as a function of plasma ion dose. The absorption peak increases as plasma ion bombardment. Extended plasma ion interaction with the surface leads to the saturation of the absorption. The characteristic of the color center formation may be described by two parameters, the initial plasma ion dose and the saturation peak absorption.[7] The former is proportional to the mean surface bond strength and the latter to the plasma ion generated defect density. Table 1 lists the initial plasma ion dose and the saturation peak absorption for various CaF_2 surfaces. The results suggest that prolonged plasma ion bombardment is required in order to generate the color center on a good surface. In addition, the saturation peak absorption increases with improved surface quality.

Table 1 Initial plasma ion dose and saturation peak absorption for various CaF_2 surfaces.

Surface processing	Polish-1	Polish-2	MRF	Cleaved
Initiated D_o ($\times 10^{15}$ cm^{-2})	3	24	33	45
Saturation peak absorption A_s (%)	16.4	21.8	29.1	33.5
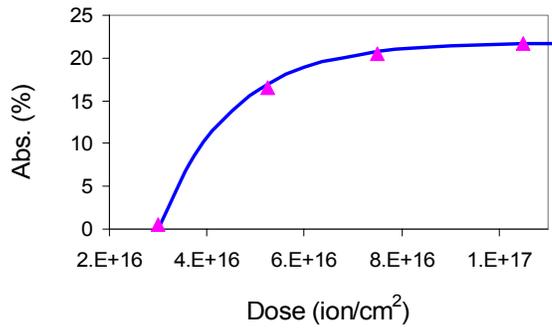
Fig. 5 Calcium colloid related peak absorption generated by low energy plasma ion
on an optically finished CaF_2 (111) surface as a function of plasma ion dose.

4. SURFACE MITIGATION

The power and repetition rate of ArF excimer laser for lithography application have been raised
from 40W to 90W, 2KHz to 6KHz over the passed a few years. Accordingly, the requirements for
optical components are drastically increased for low optical loss, high laser damage threshold and
long lifetime. The understanding of top surface and subsurface effect enables one to improve
surface finishing quality and prolong the lifetime of CaF_2 optics.
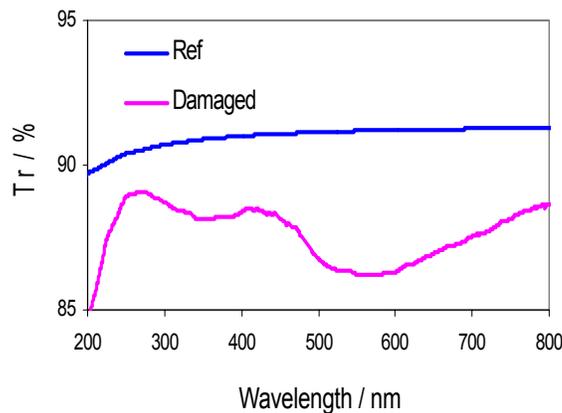
Fig. 6 Spectral transmittance of ArF excimer laser damaged CaF_2 optics,
along with the spectrum of an idea CaF_2 window labeled as Ref.

Fig. 6 plots the spectral transmittance of an ArF excimer laser damaged CaF_2 optic, along with the spectrum of an idea CaF_2 window labeled as Ref. The spectrum of the laser damaged CaF_2 optic indicates absorptions around 580nm and 350nm, corresponding to calcium colloids, F center, V_k center and H center, respectively. Comparing to the plasma ion generated shown in Fig.4, the F center related absorption is enhanced, whereas the calcium colloid related absorption is reduced in the case of the laser generated as shown in Fig. 6. The absorption difference between Fig. 4 and Fig. 6 can be explained by considering the momentum transfer in the plasma ion generated and the photo-thermal driven defect formation in the laser generated.

Further extending lifetime of fluoride optics requires additional surface mitigation, which may be accomplished by means of optical thin film coating. The surface mitigation technique presented here is to add a thin film with a hale-wavelength optical thickness (HWOT) to keep surface clean, prevent fluorine depletion and reduce surface reactivity of CaF_2 without changing optical property of the optics. Although there are several oxide and fluoride coating materials and deposition techniques are available, low optical loss and dense smooth fluorine doped SiO_2 (F-SiO_2) film is developed by means of plasma ion-assisted deposition (PIAD). The F-SiO_2 film properties, such as packing density, optical constant, microstructure and surface roughness, can be adjusted by varying the amount of plasma ion momentum transfer during deposition.[10] The understanding of the plasma ion interaction with CaF_2 surface discussed in the previous section enables one to deposit F-SiO_2 film while avoid the color center formation during PIAD process. Fig. 7 shows the AFM top image (top left) and SEM cross-sectional view (bottom left) of the F-SiO_2 film on CaF_2. The AFM image (top right) and SEM cross-sectional view of a thermal boat evaporated GdF_3 films on CaF_2 in also presented in Fig. 7 for comparison. As can been seen, the F-SiO_2 film is smooth and dense, which adding the required functionalities of the surface mitigation. The GdF_3 film, on the other hand, is porous, inhomogeneous and rough.[9]
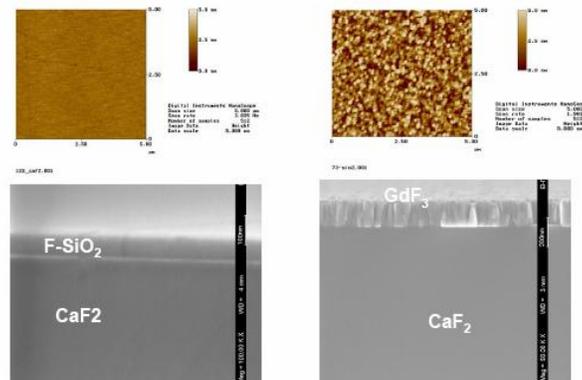
Fig. 7 AFM top images and SEM cross-sectional views of F-SiO_2 (left) and GdF_3 (right) films on CaF_2 deposited by PIAD and thermal evaporation, respectively.

Fig. 8 plots the transmittance of CaF_2 optics with and without F-SiO_2 film as a function of ArF excimer laer irradiation pulse. The laser test was performed by using an ArF laser with a rep rate of

4KHz and a fluence of 75mJ/cm^2. The optical performance of the uncoated CaF$_2$ changes rapidly during the laser test. The transmittance of the uncoated CaF$_2$ drops to 40% from 90% after 2 million pluses. Prolonged irradiation leads to a slow saturation of the degradation. On the other hand, there is no degradation in optical performance of the F-SiO$_2$ coated CaF$_2$ as shown in Fig. 8. The lifetime of the mitigated CaF$_2$ optics has been raised by a factor of 3 orders of magnitude.
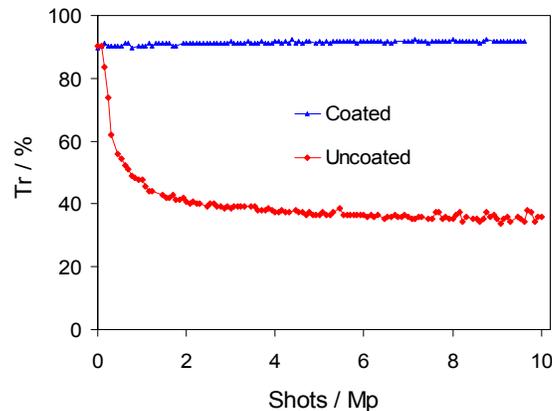
Fig. 8 Transmittance of CaF$_2$ optics with and without F-SiO$_2$ coating as a function of ArF excimer laer pulse at the condition of 75mJ/cm^2 fluence, 4KHz rep rate and 75% duty circle.

5. CONCLUSIONS

The characterization of CaF$_2$ optics suggests the existence of a top surface and a subsurface, which represents the surface roughness and the subsurface damage as a result of optical finishing, respectively. The predicted subsurface damage has been confirmed by means of MRF iterations and etching. The plasma ion generated color centers are correlated to the surface quality of CaF$_2$ and are compared to the laser generated. Dense and smooth F-SiO$_2$ coating extends the lifetime of CaF$_2$ optics by a factor of 1000.

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Q During your long term irradiation test, at what fluence level did you irradiate your calcium fluoride sample?

A It's 80 millijoules per centimeter squared. The laser frequency position is stable and duty cycle is 75%.

Q You immersed your sample in water and then looked at the surface roughness, but often its water vapor that is more significant. Did you do any high humidity tests to see how well it sealed the surface from very humid air?

A Personally, I didn't do such an experiment, but some people at our facility performed a similar test.

Q Have you looked at the composition of the surface using a more sensitive technique rather than SEM to look at the composition and behavior of your surface and the change in the surface, such as X-ray photo electron spectroscopy or Auger analysis?

A You mean the coating or the calcium-fluoride surface?

Q Actually, I meant both.

A Yes, there is a different coating sitting on the calcium fluoride surface and there are environmental substances like hydrocarbon, and things like that, so that is another reason we want to use F-doped silica, because it's high purity and amorphous, it's dense, and it isolated the calcium fluoride surface from the atmosphere.

Q I see you did some temperature dependence tests to show the in-growth of the absorption of the calcium colloids. If you go to a bit higher temperature, you will see that the colloids become unstable. In other words, if you irradiate at higher temperature it's harder to make those color centers. You may want to carry it up to 180 or 190 degrees C and you might see that happen.

A That's a good point, thank you.